

On the Velocities of Ions in Dried Gases.

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An account was recently given of a method by which the velocities of both positive and negative ions produced by Röntgen rays could be measured in very dry gases,* and some measurements were given for ions in air. These measurements have now been extended to the cases of carbon dioxide and hydrogen, and some calculations, based on the work of Townsend,† show that, while the positive ions retain a large envelope of matter even under the influence of a fairly large field of force, the negative ions become considerably diminished in size when their velocity is increased either by an increased force or by diminished pressure.

While these results are in general accord with those of other observers, yet the point which has hitherto escaped notice is that the negative ions are far more readily deprived of their customary envelope in a very dry gas than in a comparatively moist atmosphere.

In the paper already cited it was shown that the velocity of ions in air is a function of X/p , where X is the potential gradient, and p the pressure of air in the apparatus, and that this function is independent of the actual values of either X or p , but is considerably affected by minute traces of moisture. This result has been confirmed for ions in hydrogen and in carbon dioxide, and evidence has been obtained that the velocities of negative ions in air are affected by traces of carbon dioxide, while those in hydrogen are considerably lowered by traces of air.

These facts may be compared with the observations of Franek and Pohl,‡ who have shown that the velocities of negative ions in nitrogen and argon are very considerably lowered by moisture and other impurities. Unfortunately these workers used Rutherford's method of estimating the mobilities of ions, and this involves the use of an alternating E.M.F. which is a sine function of the time. As our experiments have shown that the velocity of a negative ion is not a linear function of X (at constant pressure), it is

* R. T. Lattey, 'Roy. Soc. Proc.,' 1910, A, vol. 84, p. 173.

† 'Phil. Trans.,' 1900, A, vol. 193, p. 139; 'Roy. Soc. Proc.,' 1908, A, vol. 81, p. 464; 1911, A, vol. 85, p. 25.

‡ 'Ber. der Deutsch. Phys. Ges.,' 1907, pp. 69, 194; 1909, p. 397; 1910, pp. 213, 291.

impossible to deduce true values of the ionic velocities from Franck and Pohl's observations.

Apparatus.—The apparatus used was the same as that described in the paper quoted above, with the exception that the soda lime tube (H, p. 175) was removed before carbon dioxide was admitted.

It was found to be far more difficult to dry an apparatus containing carbon dioxide than one containing other gases; this is probably owing to slowness of diffusion. In the experiments with hydrogen it was found necessary always to use freshly prepared gas, especially at low pressures, since gas which had been in the apparatus some days gave inconsistent results, presumably owing to the infiltration of minute traces of air, or to small quantities of other gases from the grease of stopcocks and similar sources.

Results.

(1) *Positive Ions.*—As in the case of air, it was found that the velocities of positive ions in carbon dioxide were proportional to X/p over the range of forces and pressures that were used. The velocities of positive ions in dried hydrogen appear from our results to increase slightly with X/p . The results are shown in the following tables:—

Table I.—Velocities of Positive Ions in Dried Hydrogen.

No.*	p (mm.).	X (volts per cm.).	X/p .	v (cm. per sec.).	vp/X .
1 H. T. T.	72.0	2.71	0.0376	140	3730
2 R. T. L.	54.9	1.93	0.0352	135	3860
3 "	54.9	2.26	0.0411	159.5	3880
4 "	46.6	2.26	0.0485	192	3960
5 "	40.0	2.24	0.0560	208	3710
6 H. T. T.	36.0	2.51	0.070	257	3780
7 R. T. L.	34.3	2.24	0.0654	289	4410
8 H. T. T.	29.1	2.69	0.092	360	3910
9 "	29.1	2.34	0.080	320	3980
10 "	21.5	2.04	0.095	385	4070
11 "	19.7	2.00	0.101	441	4340
12 "	10.0	2.03	0.203	850	4180
13 "	5.35	1.13	0.211	1020	4950
Mean.....					4058

* Initials indicate the observer responsible for the experiment.

Table II.—Velocities of Positive Ions in Dried Carbon Dioxide.

No.	p .	X.	X/p .	v .	vp/X .
1 R. T. L.	12·9	2·86	0·222	139	626
2 „	12·9	2·92	0·226	148	655
3 „	13·7	2·62	0·191	117·8	616
4 „	11·5	2·62	0·227	150·5	663
5 „	6·7	1·26	0·188	118·5	630
6 „	6·7	1·54	0·227	144	635
7 „	6·7	1·815	0·271	187·5	691
8 „	6·7	2·07	0·309	205	664
9 „	6·7	2·36	0·352	226	641
10 H. T. T.	5·53	2·26	0·409	255	623
11 „	3·68	1·66	0·451	295	654
12 „	3·68	1·94	0·527	344	653
13 „	3·68	2·24	0·609	361	593
Mean.....					642

Table III.—Velocities of Positive Ions in Moist Carbon Dioxide. (H. T. T.)

No.	p .	X.	X/p .	v .	vp/X .
1	7·56	2·14	0·283	175	618
2	7·0	2·30	0·329	200	609
3	6·47	2·23	0·345	208	624
4	5·28	2·09	0·396	235	596
5	3·71	1·66	0·447	284	635
Mean.....					616

The following table contains the values of vp/X obtained by other observers :—

Observers.	Air.		CO ₂ .		H ₂ .	
	Dry.	Moist.	Dry.	Moist.	Dry.	Moist.
L. and T.	1121	780	642	616	4058	
Langevin	1100	—	—	654	—	
Zeleny	1040	1030	578	622	5090	4030
Wellisch	1170	—	—	616	—	
Chattock	1071	996	—	631	—	4105
Chattock and Tyndall	—	—	—	—	—	4310
Phillips	—	1060	—	—	—	
Przibram	908	841	—	—	—	
Franck and Pohl	1360	1004	—	—	—	
Blanc	965	1130	630	667	—	4050

It may be mentioned that Zeleny's and Blanc's observation, that positive ions travel faster in moist than in dry carbon dioxide, could not be confirmed.

(2) *Negative Ions*.—As in the case of air, it was found that the velocity of negative ions in dried carbon dioxide and in dried hydrogen increases more rapidly than X/p , as is shown by the following tables of results:—

Velocities of Negative Ions in Carbon Dioxide. Series *a*. Imperfectly Dried. (R. T. L.)

No.	p .	X.	X/p .	v .
1	32.2	2.60	0.0807	73.7
2	32.2	2.92	0.0905	74.2
3	27.8	2.59	0.093	83
4	27.8	2.89	0.1075	87.3
5	24.6	2.58	0.105	86.3
6	24.6	2.92	0.1185	99.7
7	19.4	2.92	0.150	122.5
8	16.2	2.54	0.157	147
9	16.2	2.86	0.1765	159
10	15.3	1.74	0.114	103
11	15.3	2.01	0.131	127.5
12	15.3	2.83	0.185	174
13	11.55	1.73	0.150	138
14	11.55	2.00	0.173	157.5
15	9.9	1.035	0.105	87

Further observations showed that the value of v corresponding to any particular value of X/p was increasing as the moisture was being absorbed, and a week later the following results were obtained:—

Series *b*.

No.	p .	X.	X/p .	v .
1	11.25	1.78	0.158	368
2	9.2	2.20	0.239	2800+
3	8.9	1.10	0.1235	145
4	8.9	1.36	0.1525	235.5
5	6.7	0.90	0.134	118.5
6	5.81	0.585	0.101	97
7	5.81	1.17	0.202	2000
8	5.85	1.43	0.245	9000

A fresh quantity of CO_2 was then admitted, and another set of measurements were made (Series *c*). Between Series *c* and *d*, and also between *d* and *e*, the apparatus was exhausted and refilled with gas which had stood for some days in contact with phosphorus pentoxide.

Series *c*, *d*, and *e*.

No.	<i>p</i> .	X.	X/ <i>p</i> .	<i>v</i> .
1 <i>c</i>	19·2	2·57	0·134	122
2 <i>c</i>	18·4	2·30	0·127	122
3 <i>c</i>	18·4	2·59	0·141	159
4 <i>c</i>	16·6	2·30	0·138	162
5 <i>c</i>	15·0	2·30	0·153	344
1 <i>d</i>	15·9	2·54	0·160	418
2 <i>d</i>	15·1	2·56	0·169	1270
3 <i>d</i>	15·74	1·99	0·126	117
4 <i>d</i>	15·74	2·30	0·146	192
5 <i>d</i>	15·74	2·30	0·146	234
6 <i>d</i>	15·74	2·56	0·162	539
7 <i>d</i>	14·0	1·99	0·142	197·5
8 <i>d</i>	14·0	2·27	0·162	500
9 <i>d</i>	14·3	2·56	0·179	1435
10 <i>d</i>	13·1	1·715	0·131	135
11 <i>d</i>	13·1	2·015	0·154	354
12 <i>d</i>	13·0	2·20	0·1735	1270
1 <i>e</i>	13·4	1·14	0·0855	70
2 <i>e</i>	12·0	1·16	0·0965	102
3 <i>e</i>	11·35	1·44	0·127	150
4 <i>e</i>	11·35	1·70	0·150	297

Velocities of Negative Ions in Dried Hydrogen. Series *a*. Imperfectly Dried.

No.	<i>p</i> .	X.	X/ <i>p</i> .	<i>v</i> .	<i>vp</i> /X.
1	160·0	2·39	0·0149	89·2	5987
2	150·0	2·39	0·0159	98·4	6189
3	135·2	2·39	0·01695	106·7	6295
4	135·2	2·09	0·01545	97·2	6292
5	135·2	2·60	0·0192	129·6	6750
6	135·2	2·97	0·0220	165·0	7500
7	124·5	2·34	0·0188	122·5	6516
8	124·5	2·63	0·0211	138	6540
9	124·5	2·64	0·0212	146	6886
10	124·5	2·92	0·02345	153	6525
11	106·8	2·04	0·0191	125	6544
12	106·8	2·60	0·02435	165	6776
13	94·0	2·03	0·0216	135	6250
14	93·1	2·34	0·0252	170	6746
15	93·1	2·60	0·0279	194·2	6960

These results were obtained with the first filling of gas, after washing out the apparatus several times, and are possibly affected by minute traces of CO₂. They are given here to show the extraordinary effect of small traces of impurity—less than 1 in 1000 probably. The following results were obtained with several different samples of dried hydrogen:—

No.	p .	X.	X/p .	v .
1	197·6	2·57	0·0130	102
2	171·8	2·29	0·0133	104·5
3	171·8	2·57	0·0150	149
4	171·8	2·58	0·0151	141
5	154·2	2·29	0·0148	138
6	154·2	2·57	0·01665	180
7	92·2	2·00	0·0217	500
8	92·2	2·56	0·0278	1475
9	90·6	1·44	0·0159	119
10	90·6	1·745	0·0193	330
11	82·5	1·44	0·0175	141
12	82·5	2·57	0·0311	2080
13	73·6	0·83	0·0113	84·3
14	73·6	1·69	0·0229	475
15	73·2	1·10	0·0150	170
16	73·2	1·415	0·0193	310
17	67·6	1·415	0·0209	445
18	67·6	1·43	0·0211	451
19	67·6	1·44	0·0214	406
20	67·6	1·715	0·0253	1019
21	67·6	1·74	0·0259	1141
22	67·3	1·69	0·0251	825
23	66·9	0·83	0·0124	114
24	66·9	1·13	0·0169	220

All these results are shown graphically in figs. 1 and 2. It will be seen that the curves all have the same general shape. The following tables, which have been compiled from the mean curves, show the velocities corresponding to various values of X/p :—

Carbon Dioxide—

X/p	0·08	0·09	0·10	0·11	0·12	0·13	0·14	0·15	0·16	0·17
v	64	73	82	92	106	132	182·5	277	468	977

Hydrogen—

X/p	0·010	0·012	0·014	0·016	0·018	0·020	0·022	0·024	0·026	0·027
v	68	95	127	174	236	336	489	730	1100	1347

In all cases, the velocities for comparatively small values of X/p approximate to a linear function of that quantity. The values of vp/X for these small values of X/p may be compared with those obtained by other observers :—

Observers.	H_2 .		CO_2 .	
	Moist.	Dry.	Moist.	Dry.
L. and T.	—	6170	—	800
Zeleny	4255	6040	570	615
Rutherford	2965	—	593	—
Kovarik	—	—	612	770
Wellisch	—	—	624	—
Langevin	—	—	683	—
Blanc	—	7600	644	783
Chattock	—	5650	703	—
Chattock and Tyndall	—	5455	—	—

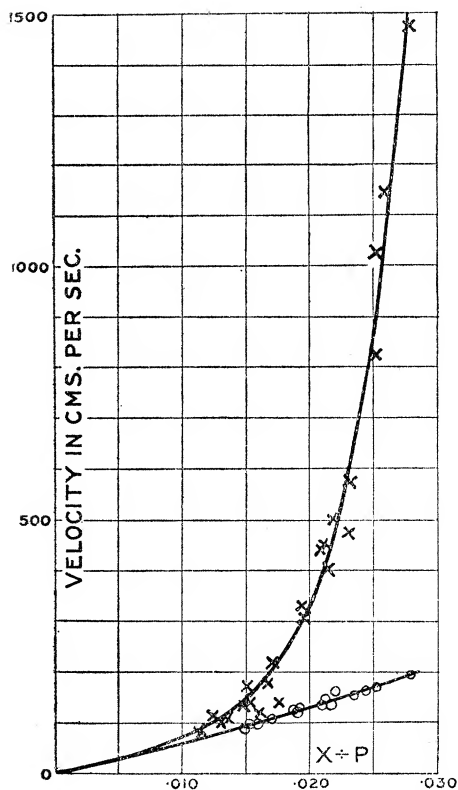


FIG. 1.—Hydrogen.

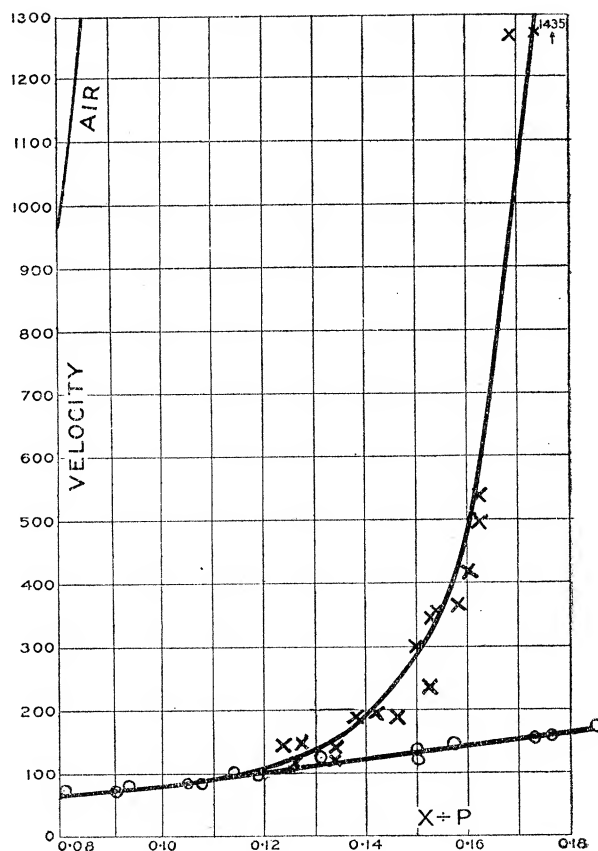


FIG. 2.—Carbon dioxide.

x dry. o moist.

Discussion of Results.

Since the positive ions show a linear relationship between v and X/p , the ordinary formula

$$D = \frac{\Pi v'}{NeX}, \text{ or } D = 3.21 \times 10^{-5} \frac{vp}{X}$$

may be applied, where D is the diffusion coefficient between the ions and the gas in which they are moving with velocity v' at atmospheric pressure (Π).^{*} From this, an approximate value for the molecular masses of the ions may be obtained by using the formula $D^2 m_1 m_2 = K^2$; m_1 and m_2 being the molecular masses of the gases between which diffusion is taking place, and K being a constant. Comparison of the available data for gases gives an average value for K of about 4.6, when the molecular masses are in the ordinary chemical units.

^{*} Townsend, 'Phil. Trans.,' 1900, A, vol. 193, p. 129.

	$vp/X.$	D.	$m.$
Air	1121	0·0360	564
CO ₂	642	0·0205	1144
Hydrogen	4058	0·1303	624

It appears therefore that the positive ion has a large mass, and is probably an aggregate of at least 25 molecules of the gas in which it is formed, clustered round an electronic nucleus.

In moist gases, and in dried gases with small values of X/p , a similar calculation can be made, but with higher values of X/p the velocities are not linear functions of this ratio. But Townsend has shown that to obtain the true values of D in these cases, the quantity $\Pi v'/NeX$ must be multiplied by $\sqrt{k}$, where k is a factor which can be deduced from his experiments on the lateral diffusion of a narrow stream of ions in an electric field of force.* The complete equation for determining the molecular mass of a negative ion thus becomes

$$m = \frac{K^2 (NeX)^2}{k (\Pi v')^2 m_1}.$$

Unfortunately, it is only in the case of air that any values of k are given. In the case of other gases it is only possible to give calculations of mk , where k may have any value greater than unity, but probably less than 10.

Air.

$X/p.$	$vp/X.$	D.	$k.$	$m.$
0·04	2812	0·1009	1·25	72
0·05	3462	0·1295	1·36	43·5
0·06	4797	0·1875	1·48	21
0·07	7293	0·2950	1·59	8·5
0·08	11920	0·5005	1·71	2·5
0·09	20500	0·890	1·83	0·9

CO₂.

Hydrogen.

$X/p.$	$vp/X.$	$Dk^{-\frac{1}{2}}.$	$mk.$	$X/p.$	$vp/X.$	$Dk^{-\frac{1}{2}}.$	$mk.$
0·08	800	0·0257	725	0·010	6800	0·2183	221
0·09	810	0·0260	708	0·012	7917	0·2541	163
0·10	820	0·0263	692	0·014	9070	0·2912	124
0·11	836	0·0268 ₅	664	0·016	10875	0·3491	86·5
0·12	883	0·0283 ₅	596	0·018	13110	0·421	59·5
0·13	1015	0·0326	450	0·020	16800	0·539	36
0·14	1304	0·0418 ₅	273	0·022	22230	0·7135	21
0·15	1847	0·0593	136	0·024	30420	0·976	11
0·16	2925	0·0939	54	0·026	42310	1·358	6
0·17	5747	0·1845	14·5	0·027	49880	1·601	4

* Roy. Soc. Proc., 1911, A, vol. 85, p. 28.

It would appear, therefore, that a negative ion in a dried gas has, like a positive ion, an envelope of molecules about its electronic nucleus, and that when a certain velocity is exceeded the electron is partially deprived of this envelope by its collision with the molecules of the gas. This will increase its mobility in two ways: (1) on account of the decreased mass of the ion its acceleration between impacts will be increased; (2) its decreased radius will give it a greater freedom from collisions.

The values given above for the molecular mass must, therefore, be regarded as the average value of the mass of the group of molecules associated with the electron. Since this mass becomes smaller than that of an air or CO₂ molecule—and probably also than that of a hydrogen molecule—it is clear that in these gases the electron must have free existence during some part of its course.

The envelope of an electron may consist of water molecules or of molecules of the gas in which it is moving. This research has shown that with increasing velocities this envelope is more easily removed the fewer the water molecules present, and it would appear, therefore, probable that the envelope in dry gases consists of molecules of the gas, and that these are more easily removed than water molecules.

The researches of other investigators have shown that the negative ion appears to retain its envelope more persistently in an impure than in a pure gas, and their results may be compared with those given here.

Pure gas.	Impurity.	Authority.
Nitrogen	Oxygen	} Franck, 'Ber. der deutsch. phys. Ges.,' 1910, p. 613.
"	Chlorine	
"	Water	
Argon	Oxygen	} Franck, 'Ber. der deutsch. phys. Ges.,' 1910, p. 291.
Hydrogen	"	
Air	Water	} Chattock and Tyndall, 'Phil. Mag.' 1910, vol. 19 [6], p. 449.
Carbon dioxide	"	
Hydrogen	"	} R. T. Lattey, 'Roy. Soc. Proc.,' A, 1910, vol. 84, p. 173.
		} R. T. L. and H. T. T.